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14. ABSTRACT

This is the final report for a three-year project to identify and characterize donors and acceptors in single crystals of ZnO. Samples were obtained from our industrial partner (Eagle-Picher) and from the Air Force Research Laboratory (Hanscom AFB). The experimental techniques used to characterize the crystals were Hall effect, infrared and visible absorption, photoluminescence, thermoluminescence, electron paramagnetic resonance (EPR), and electron-nuclear double resonance (ENDOR). Studies completed during this project include: (1) an investigation of the isolated nitrogen acceptor in ZnO, (2) an investigation of the role of copper in the green luminescence from ZnO, (3) an investigation of molecular nitrogen acceptors in ZnO, (4) the diffusion of lithium acceptors into single crystals of ZnO, (5) the temperature dependence of the free exciton transition energy, (6) the ionization energy of isolated nitrogen acceptors determined from photoluminescence. (7) the observation of deep levels associated with transition-metal ions, (8) the effect of hydrogen annealing on the excitonic region of the photoluminescence spectrum, (9) the demonstration of the role of hydrogen as a charge compensator for singly ionized acceptors (i.e., the Li-OH center), and (10) the production of native donors in ZnO by high-temperature anneals in Zn vapor.

15. SUBJECT TERMS

ZnO, wide-band-gap semiconductor, electro-optic material, ultraviolet light emitter, donors, acceptors, hydrogen, Hall effect, infrared absorption, visible absorption, photoluminescence, electron paramagnetic resonance, PL, EPR

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FINAL TECHNICAL REPORT
(For period from May 15, 2002 to May 14, 2005)

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I. Project Overview

This document is the final technical report for work performed under Air Force Office of Scientific Research (AFOSR) Grant F49620-02-1-0254. This was a three-year project entitled "Optical and Magnetic Resonance Characterization of Donors and Acceptors in Zinc Oxide." The Principal Investigators were Larry E. Halliburton and Nancy C. Giles, Physics Department, West Virginia University. In this three-year research program, which started May 15, 2002, an emphasis was placed on identifying and characterizing the donors and acceptors that have thus far prevented the routine production of p-type ZnO films and crystals. During the project, fundamental spectroscopic defect studies were performed on a series of ZnO crystals grown by the seeded chemical vapor transport method at Eagle-Picher and by the hydrothermal technique at the Air Force Research Laboratory (Hanscom AFB). Crystalline ZnO is an important wide band gap semiconductor with significant promise as a uv light emitting material (rivaling GaN). However, its widespread use has been limited by the inability to routinely make p-type material.

In this project, we used the following experimental techniques to identify and characterize intentional and unintentional donors and acceptors in single crystals of ZnO: Hall effect, photoluminescence (PL), thermoluminescence, visible absorption, infrared absorption, electron paramagnetic resonance (EPR), and electron-nuclear double resonance (ENDOR). Our industrial partner was Eagle-Picher in Miami, OK.

II. Student Participation

Six graduate students have participated in this ZnO project. These are Lijun Wang, Lihua Bai, Madalina Chirila, Chunchuan Xu, Ming Luo, and Sean Evans.

Lijun Wang received his PhD in May of 2004 under the supervision of Professor Nancy C. Giles. The title of his dissertation was "Photoluminescence Study of As-Grown and Thermally Annealed Bulk ZnO Crystals." He is presently employed as post-doc at the Ferdinand-Braun Institute in Berlin.

Madalina Chirila received her PhD in December of 2003 under the direction of Professor Larry E. Halliburton. The title of her dissertation was "Characterization of Point Defects in Nonlinear Optical Materials." She is presently employed as a post-doc at the National Institute of Occupational Safety and Health (NIOSH) in Morgantown, WV.

Lihua Bai received her PhD in August of 2004 under the direction of Professor Nancy C. Giles. The title of her dissertation was "Optical Properties of $CdGeAs_2$." She is presently employed as a post-doc at Fisk University in Nashville, TN.

Lihua Bai will receive her PhD in December of 2005. Chunchuan Xu will receive his PhD in May of 2006. Sean Evans will receive his PhD in December of 2006.

III. Publications and Presentations

<u>Publications Supported by this Project:</u>

1. *"Production of Nitrogen Acceptors in ZnO by Thermal Annealing,"* N. Y. Garces, N. C. Giles, L. E. Halliburton, G. Cantwell, D. B. Eason, D. C. Reynolds, and D. C. Look, Applied Physics Letters **80**, 1334 (2002).

2. *"Role of Copper in the Green Luminescence from ZnO Crystals,"* N. Y. Garces, L. Wang, L. Bai, N. C. Giles, L. E. Halliburton, and G. Cantwell, Applied Physics Letters **81**, 622 (2002).

3. *"The Path to ZnO Devices: Donor and Acceptor Dynamics,"* D. C. Look, R. L. Jones, J. R. Sizelove, N. Y. Garces, N. C. Giles, and L. E. Halliburton, Physica Status Solidi (a) **195**, 171 (2003).

4. *"Luminescence and EPR Study of Lithium-Diffused ZnO Crystals,"* N. Y. Garces, L. Wang, M. M. Chirila, L. E. Halliburton, and N. C. Giles, Materials Research Society Symposium Proceedings **744**, 87 (2003).

5. *"Molecular Nitrogen (N_2^-) Acceptors and Isolated Nitrogen (N^-) Acceptors in ZnO Crystals,"* N. Y. Garces, L. Wang, N. C. Giles, L. E. Halliburton, G. Cantwell, and D. B. Eason, Journal of Applied Physics **94**, 301 (2003).

6. *"Thermal Diffusion of Lithium Acceptors into ZnO Crystals,"* N. Y. Garces, L. Wang, N. C. Giles, L. E. Halliburton, D. C. Look, and D. C. Reynolds, Journal of Electronic Materials **32**, 766 (2003).

7. *"Temperature Dependence of the Free-Exciton Transition Energy in Zinc Oxide by Photoluminescence Excitation,"* L. Wang and N. C. Giles, Journal of Applied Physics **94**, 973 (2003).

8. *"Determination of the Nitrogen Acceptor Ionization Energy in Zinc Oxide by Photoluminescence Spectroscopy,"* L. Wang and N. C. Giles, Applied Physics Letters **84**, 3049 (2004).

9. *"Remote Hydrogen Plasma Doping of Single Crystal ZnO,"* Y. M. Strzhemechny, H. L. Mosbacher, D. C. Look, D. C. Reynolds, C. W. Litton, N. Y. Garces, N. C. Giles, L. E. Halliburton, S. Niki, and L. J. Brillson, Applied Physics Letters **84**, 2545 (2004).

10. *"Photoluminescence and EPR of Donors and Acceptors in ZnO,"* N. C. Giles, N. Y. Garces, L. Wang, and L. E. Halliburton, SPIE Proceedings Vol. **5359**, 267 (2004).

11. *"Determination of the Nitrogen Acceptor Ionization Energy in Zinc Oxide by Photoluminescence Spectroscopy,"* L. Wang, N. Y. Garces, L. E. Halliburton, and N. C. Giles, Materials Research Society Symposium Proceedings **799**, 261 (2004).

12. *"Infrared Absorption from OH- Ions Adjacent to Lithium Acceptors in Hydrothermally Grown ZnO,"* L. E. Halliburton, L. Wang, L. Bai, N. Y. Garces, N. C. Giles, M. J. Callahan, and B. Wang, Journal of Applied Physics **96**, 7168 (2004).

13. *"Shallow Donor Generation in ZnO by Remote Hydrogen Plasma,"* Y. M. Strzhemechny, H. L. Mosbacher, S. H. Goss, D. C. Look, D. C. Reynolds, C. W. Litton, N. Y. Garces, N. C. Giles, L. E. Halliburton, S. Niki, and L. J. Brillson, Journal of Electronic Materials **34**, 399 (2005).

14. *"Production of Native Donors in ZnO by Annealing at High Temperature in Zn Vapor,"* L. E. Halliburton, N. C. Giles, N. Y. Garces, M. Luo, C. Xu, L. Bai, and L. A. Boatner, accepted by Applied Physics Letters (publication expected in October, 2005).

Presentations Supported by this Project:

1. *"The Path to p-type ZnO: Donor and Acceptor Dynamics,"* D. C Look (presenter), D. C. Reynolds, N. Y. Garces, N. C. Giles, and L. E. Halliburton, 15-minute presentation, EXMATEC (Conference on Expert Evaluation and Control of Compound Semiconductor Materials and Technologies, Budapest, Hungary, May 27, 2002.

2. *"Use of EPR to Monitor the Formation of Nitrogen and Lithium Acceptors in Thermally Annealed Bulk ZnO Crystals,"* L. E. Halliburton (presenter), N. Y. Garces, L. Wang, N. C. Giles, G. Cantwell, and D. B. Eason, 20-minute presentation, Second International Workshop on Zinc Oxide (Materials Research Society), Dayton, OH, October 24, 2002.

3. *"Photoluminescence Study of Excitonic and Visible Emission from As-Grown and Thermally Annealed Bulk ZnO Crystals,"* L. Wang (presenter), L. Halliburton, N. Garces, N. Giles, G. Cantwell, and D. Eason, 20-minute presentation, Second International Workshop on Zinc Oxide (Materials Research Society), Dayton, OH, October 24, 2002.

4. *"Characterization of Nitrogen and Lithium Acceptors in ZnO Crystals,"* L. E. Halliburton (presenter), N. C. Giles, L. Wang, N. Y. Garces, D. C. Look, and D. C. Reynolds, 15-minute presentation, U.S. Workshop on the Physics and Chemistry of II-VI Materials, San Diego, CA, November 14, 2002.

5. *"Photoluminescence and EPR Study of Thermally Annealed Bulk Zinc Oxide Crystals,"* Lijun Wang, N. Y. Garces, L. E. Halliburton, and N. C. Giles (presenter), 15-minute presentation, Materials Research Society Fall Meeting, Boston, MA, December 3, 2002.

6. *"Characterization of Donors and Acceptors in ZnO,"* N. C. Giles (presenter) and L. E. Halliburton, 30-minute presentation, Air Force Semiconductor Materials Program Review, Williamsburg, VA, June 9, 2003.

7. *"Photoluminescence and EPR of Donors and Acceptors in Bulk ZnO Single Crystals,"* N. C. Giles (presenter), 60-minute seminar, Air Force Research Laboratory, Wright-Patterson AFB, Dayton, OH, July 9, 2003.

8. *"Photoluminescence Study of Bulk ZnO Crystals,"* Lijun Wang (presenter), N. Y. Garces, L. E. Halliburton, and N. C. Giles, 15-minute presentation, Third International Symposium on Laser and NLO Materials, Keystone, CO, July 22, 2003.

9. *"Determination of the Nitrogen Acceptor Ionization Energy in ZnO by Photoluminescence Spectroscopy,"* Lijun Wang, N. Y. Garces, L. E. Halliburton, and N. C. Giles (presenter), poster

presentation, Annual Meeting of the Materials Research Society (MRS), Boston, MA, December 2, 2003.

10. *"Photoluminescence and EPR of Donors and Acceptors in ZnO,"* N. C. Giles (presenter), N. Y. Garces, Lijun Wang, and L. E. Halliburton, 25-minute invited oral presentation, Photonics West, Annual SPIE Conference, San Jose, CA, January 27, 2004.

11. *"EPR, PL, and Absorption Experiments: Characterization of Donors and Acceptors in ZnO,"* L. E. Halliburton (presenter) and N. C. Giles, 20-minute oral presentation, AFOSR Zinc Oxide Workshop, Maui, Hawaii, May 17, 2004.

12. *"Remote Hydrogen Plasma Doping of Single Crystal ZnO,"* Y. M. Strzhemechny (presenter), D. C. Look, D. C. Reynolds, C. W. Litton, N. Y. Garces, N. C. Giles, L. E. Halliburton, S. Niki, and L. J. Brillson, 20-minute oral presentation, 2004 TMS Electronic Materials Conference, Notre Dame, IN, June 23, 2004.

13. *"EPR and Optical Characterization of ZnO Crystals,"* L. E. Halliburton (presenter), 30-minute invited oral presentation, E-MRS (European Materials Research Society), Symposium G: ZnO and Related Materials, Strasbourg, France, June 1, 2005.

IV. ZnO Results Obtained at West Virginia University

The following paragraphs in this section provide summaries of ZnO papers published by our group at West Virginia University as a result of this AFOSR funding. Note that several of these studies have been co-authored with research investigators at the Air Force Research Laboratory (Wright-Patterson AFB and Hanscom AFB) and our industrial partner (Eagle-Picher).

A. Identification of Isolated Nitrogen Acceptors

Applied Physics Letters 80, 1334 (2002). Nitrogen acceptors are formed when undoped single crystals of zinc oxide (ZnO) grown by the chemical-vapor transport method are annealed in air or nitrogen atmosphere at temperatures between 600 and 900 °C. After an anneal, an induced near-edge absorption band causes the crystals to appear yellow. Also, the concentration of neutral shallow donors, as monitored by electron paramagnetic resonance (EPR), is significantly reduced. A photoinduced EPR signal due to neutral nitrogen acceptors is observed when the annealed crystals are exposed to laser light (e.g., 364, 442, 458, or 514 nm) at low temperature. The nitrogens are initially in the nonparamagnetic singly ionized state (N^-) in an annealed crystal, because of the large number of shallow donors, and the light converts a portion of them to the paramagnetic neutral acceptor state (N^0). [Authors are N. Y. Garces, N. C. Giles, L. E. Halliburton, G. Cantwell, D. B. Eason, D. C. Reynolds, and D. C. Look.]

B. Role of Copper Acceptors in the Green Luminescence

Applied Physics Letters 81, 622 (2002). Electron paramagnetic resonance (EPR), photoluminescence, and infrared optical absorption have been used to investigate a ZnO crystal before and after a thermal anneal for 1 h in air at 900 °C. The sample was an undoped high quality crystal grown by the chemical vapor transport method. In addition to shallow donor impurities, the crystal contained trace amounts of copper ions. Prior to the thermal anneal, these ions were all in the Cu^+ ($3d^{10}$) state and the observed luminescence at 5 K, produced by 364 nm light, consisted of a broad structureless band peaking at 500 nm. After the high-temperature anneal, the Cu^{2+} ($3d^9$) EPR spectrum was observed and the luminescence had changed significantly. The emission then peaked near 510 nm and showed structure identical to that reported by Dingle [Phys. Rev. Lett. **23**, 579 (1969)]. Our data reaffirm that the structured green emission in ZnO is associated with Cu^{2+} ions. We suggest that the unstructured green emission (observed before the high-temperature anneal) is donor–acceptor pair recombination involving the Cu^+ acceptors. [Authors are N. Y. Garces, L. Wang, L. Bai, N. C. Giles, L. E. Halliburton, and G. Cantwell.]

C. Identification of Nitrogen-Nitrogen Acceptor Complexes

Journal of Applied Physics 94, 519 (2003). Electron paramagnetic resonance (EPR) has been used to investigate molecular nitrogen and isolated nitrogen acceptors in single crystals of ZnO. These samples were grown by the seeded chemical vapor transport method with N_2 added to the gas stream. A five-line EPR spectrum is observed at low temperature in the as-grown bulk crystals and is assigned to N_2^- molecules substituting for oxygen. This structure arises from nearly equal hyperfine interactions with two nitrogen nuclei (^{14}N, 99.63% abundant, I = 1). The spin Hamiltonian parameters for the N_2^- center are $g_{\parallel} = 2.0036$, $g_{\perp} = 1.9935$, $A_{\parallel} = 9.8$ MHz, and $A_{\perp} = 20.1$ MHz, with the unique directions parallel to the c axis. Laser excitation at 9 K, with 325 or 442 nm light, eliminates the N_2^- spectrum (when the N_2^- convert to N_2^0) and independently introduces the EPR spectrum due to isolated nitrogen acceptors (when N^- acceptors convert to N^0). Removing the laser light and warming to approximately 100 K restores the crystal to its pre-illuminated state. In separate experiments, heating between 600 and 800°C increases the number of N_2^- and N^0 acceptors that can be observed. We suggest that the activation of these nitrogen acceptors occurs when complexes of hydrogen and nitrogen thermally dissociate. Further heating above 800°C drives the two nitrogen acceptors to inactive forms. Our results thus provide direct support for the concept of thermal activation of acceptors in ZnO crystals. [Authors are N. Y. Garces, L. Wang, N. C. Giles, L. E. Halliburton, G. Cantwell, and D. B. Eason.]

D. Temperature Dependence of the Free-Exciton Emission

Journal of Applied Physics 94, 973 (2003). Photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopies are used to track the temperature dependence of the *A* exciton energy (E_{XA}) in undoped bulk ZnO crystals grown by the seeded-chemical-vapor-transport method. For T>150 K, the edge emission becomes broad as the A exciton recombination and its longitudinal-optical (LO) phonon replica become superimposed. We use PLE to determine the temperature dependence of E_{XA} by monitoring the broad green emission commonly observed in as-grown ZnO crystals, and thus have established the energy difference between the E_{XA} and PL emission peak energies. The PL emission at 3.26 eV at room temperature is shown to be offset by about 50 meV to lower energy than the actual E_{XA} transition. The temperature dependence of the energy difference between the E_{XA} and PL peaks is compared with predictions based on the lineshape function for the E_{XA} – LO recombination. At 300 K, the PL is predominantly composed of E_{XA} – LO recombination. Further, the temperature dependence of the E_{XA} transition energy can be described using standard expressions and the Debye and Einstein temperatures are found to be 700±30 and 240±5 K, respectively. The slope of the E_{XA} versus *T* curve for ZnO approaches a constant value of $dE_{XA}/dT = -0.35$ meV/K near room temperature. [Authors are N. C. Giles and L. Wang.]

E. In-Diffusion of Substitutional Lithium Acceptors

Journal of Electronic Materials 32, 766 (2003). Electron paramagnetic resonance (EPR) has been used to monitor the diffusion of lithium ions into single crystals of ZnO. The in-diffusion occurs when a crystal is embedded in LiF powder and then held in air at temperatures near 750°C for periods of time ranging up to 22 hours. These added lithium ions occupy zinc sites and become singly ionized acceptors (because the material is initially n type). A corresponding reduction in the number of neutral shallow donors is observed with EPR. To monitor the lithium acceptors, we temporarily convert them to the EPR-active neutral acceptor state by exposure to laser light (325 or 442 nm) at low temperatures. Also, after each diffusion treatment, we monitor the EPR signal of singly ionized copper acceptors and the photoinduced EPR signal of neutral nitrogen acceptors. These nitrogen and copper impurities are initially present in the crystal, at trace levels, and are made observable by the thermal anneals. Infrared absorption measurements at room temperature in the 2 to 10 μm region show that the concentration of free carriers decreases as lithium is added to the crystal. After 22 hours at 750°C in the LiF powder, the free carrier absorption is no longer present and the crystal is semi-insulating. No evidence was found to suggest that lithium formed stable interstitial centers in bulk ZnO. [Authors are N. Y. Garces, L. Wang, N. C. Giles, L. E. Halliburton, D. C. Reynolds, and D. C. Look.]

F. Luminescence Associated with Ni and Fe Deep Donors

Materials Research Society Symposium Proceedings <u>744</u>, 87 (2003). Zinc oxide (ZnO) crystals grown by the seeded chemical vapor transport method have been studied using photoluminescence(PL), thermoluminescence (TL), and electron paramagnetic resonance (EPR) techniques. Lithium acceptors were diffused into the crystals during anneals in LiF powder at temperatures in the 750 to 850°C range. After a lithium diffusion, EPR was used to monitor neutral lithium acceptors and neutral shallow donors, as well as Ni^{3+}, Fe^{3+}, and Cu^{2+} impurities unintentionally present. Excitonic and deep-level PL emissions were also monitored before and after these diffusions. Two broad overlapping TL emission bands were observed at 117 and 145 K when a Li-diffused crystal was illuminated at 77 K with 325-nm light and then rapidly warmed to room temperature. The two TL bands have the same spectral dependence (the peak in wavelength is 540 nm when the intensity of the light reaches a maximum). These "glow" peaks occur when electrons are thermally released from Ni^{2+} and Fe^{2+} ions and recombine with holes at neutral lithium acceptors. [Authors are N. Y. Garces, L. Wang, M. M. Chirila, L. E. Halliburton, and N. C. Giles.]

G. Ionization Energy of Substitutional Nitrogen Acceptors

Applied Physics Letters <u>84</u>, 3049 (2004). Photoluminescence spectroscopy of nitrogen-related emissions in ZnO is used to establish the ionization energy of the substitutional nitrogen acceptor. The temperature dependence of the nitrogen-related electron-acceptor (e,A^0) emission band has been monitored in as-grown single crystals of ZnO. Line shape analysis of this band is used to determine the acceptor ionization energy. The temperature dependence of the band gap for ZnO was included in our analysis and the low-temperature acceptor ionization energy for substitutional nitrogen at an oxygen site in ZnO was found to be $E_A = 209\pm3$ meV. Our line shape analysis indicates a small temperature-dependent decrease in E_A for $T>5$ K. [Authors are L. Wang and N. C. Giles.]

H. Effects of Hydrogenation on PL and Surface Conductivity

Applied Physics Letters <u>84</u>, 2545 (2004). We demonstrate that remote plasma hydrogenation can increase electron concentrations in ZnO single crystals by more than an order of magnitude. We investigated the effects of this treatment on Hall concentration and mobility as well as on the bound exciton emission peak I_4 for a variety of ZnO single crystals – bulk air annealed, Li doped, and epitaxially grown on sapphire. Hydrogen increases I_4 intensity in conducting samples annealed at 500 and 600 °C and partially restores emission in the I_4 range for Li-diffused ZnO. Hydrogenation increases carrier concentration significantly for the semi-insulating Li doped and epitaxial thin film samples. These results indicate a strong link between the incorporation of hydrogen, increased donor-bound exciton PL emission, and increased *n*-type conductivity. [Authors are Y. M. Strzhemechny, H. L. Mosbacher, D. C. Look, D. C. Reynolds, C. W. Litton, N. Y. Garces, N. C. Giles, L. E. Halliburton, S. Niki, and L. J. Brillson.]

I. Charge Compensation of Lithium Acceptors by OH Ions

Journal of Applied Physics 96, 7168 (2004). An intense infrared absorption band has been observed in a hydrothermally grown ZnO crystal. At 12 K, the band peaks near 3577.3 cm^{-1} and has a half width of 0.40 cm^{-1} and, at 300 K, the band peaks at 3547 cm^{-1} and has a half width of 41.3 cm^{-1}. This absorption band is highly polarized, with its maximum intensity occurring when the electric field vector of the measuring light is parallel to the c axis of the crystal. Photoinduced electron paramagnetic resonance experiments show that the crystal contains lithium acceptors (i.e., lithium ions occupying zinc sites). Lithium and OH^- ions are present in the crystal because lithium carbonate, sodium hydroxide, and potassium hydroxide are used as solvents during the hydrothermal growth. In the as-grown crystal, some of the lithium acceptors will have an OH^- ion located at an adjacent axial oxygen site (to serve as a passivator), and we assign the 3577.3 cm^{-1} band observed at 12 K to these neutral complexes. Our results illustrate the role of hydrogen as a charge compensator for singly ionized acceptors in ZnO. [Authors are L. E. Halliburton, L. Wang, L. Bai, N. Y. Garces, N. C. Giles, M. J. Callahan, and B. Wang.]

J. Production of Native Donors by Annealing in Zn Vapor

Applied Physics Letters 87, to appear in October, 2005. Zinc oxide crystals grown by the seeded chemical vapor transport method have been annealed in zinc vapor at 1100 °C for 30 min. These thermochemical reduction treatments produce a deep red coloration in the crystals and increase their n-type electrical conductivity. Electron paramagnetic resonance (EPR), optical absorption, and Hall measurements were used to monitor changes in the crystals. After an anneal, an intense optical absorption band is present that extends from the band edge out to approximately 550 nm, and the EPR signal near $g = 1.96$ (due to shallow donors and/or conduction-band electrons), the free-carrier absorption, and the Hall electron concentration are all larger. Hydrogen was not present during these anneals, thus leaving oxygen vacancies and zinc interstitials as candidates for the added donors. Neutral oxygen vacancies are produced at high temperature by the additive-coloration mechanism, and are responsible for the broad near-edge absorption band. The observed increase in the number of free carriers is a result of either (1) the formation of zinc interstitials or (2) having the ground state of the neutral oxygen vacancy near the conduction band. This study has demonstrated the efficiency of the thermochemical reduction process in modifying the optical and electrical properties of ZnO by introducing native donors, and it has established an optical "signature" for the presence of oxygen vacancies in ZnO. [Authors are L. E. Halliburton, N. C. Giles, N. Y. Garces, M. Luo, C. Xu, L. Bai, and L. A. Boatner.]